

Exact solutions of kinetic equations in an autocatalytic growth model

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Kinetic equations are introduced for the transition-metal nanocluster nucleation and growth mechanism, as proposed by Watzky and Finke. Equations of this type take the form of Smoluchowski coagulation equations supplemented with the terms responsible for the chemical reactions. In the absence of coagulation, we find complete analytical solutions of the model equations for the autocatalytic rate constant both proportional to the cluster mass, and the mass-independent one. In the former case, $\xi_k = s_k(\xi_1) \propto \xi_1^k/k$ was obtained, while in the latter, the functional form of $s_k(\xi_1)$ is more complicated. In both cases, $\xi_1(t) = h_\mu(M_\mu(t))$ is a function of the moments of the mass distribution. Both functions, $s_k(\xi_1)$ and $h_\mu(M_\mu)$, depend on the assumed mechanism of autocatalytic growth and monomer production, and not on other chemical reactions present in a system.

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Nucleation and growth phenomena, resulting in occurrence of a new phase from a homogeneous host phase, are ubiquitous in nature [1, 2]. In many cases, apart from processes of coagulation and fragmentation, chemical reactions are also present in a system. Frequently, the chemical reactions account for phenomena studied by polymer and colloidal science.

Nucleation and subsequent growth of metal nanoclusters in aqueous solution is a topic of considerable current interest, since solution route synthesis is one of the most convenient methods of producing transition-metal nanoparticles [3]. However, applicability of this method depends on the ability to control size and shape of the produced nanoparticles, which determine their unique optical, electronic and catalytic properties. For that reason, theoretical models capable of predicting the cluster size distribution, as well as its dependence on the experimentally controllable parameters of the system, are required.

A mechanism of transition-metal colloidal nanoparticle formation has been proposed by Watzky and Finke [4], cf. [5–8]. The WF mechanism consists of (i) slow monomer, i.e., the zerovalent transition-metal atom (B_1) production due to reduction reaction $A \rightarrow B_1$ of a metal precursor (A), usually a transition-metal complex coordination compound, (ii) fast autocatalytic reduction reaction $A + B_i \rightarrow B_{i+1}$ taking place on the surface of growing metal nanoparticles, consisting of i atoms (B_i), and (iii) process of coagulation $B_i + B_j \rightleftharpoons B_{i+j}$, reversible or otherwise. In the original WF scheme [4], step (iii) had not been considered. Irreversible coagulation was first introduced in [5].

For the transition metals in which higher oxidation states are present, e.g. Au, at least one additional preliminary step of the form (iv) $P \rightarrow A$ is needed [9–13].

As an excess of the reducing agent is usually used in the reactions (i), (ii), (iv), its concentration is fairly time-independent, and all chemical reactions may be treated

as irreversible. Furthermore, (i) and (iv) may be treated as reactions of pseudo-first order, while (ii) as a reaction of pseudo-second order.

The WF mechanism is applicable to other systems. Certain cases of transition metal oxides or sulfides nanocluster formation, or polymerization phenomena of various kind, including protein aggregation [8], are well described by an effective model defined by (i)–(iv), even if the actual mechanism of nucleation and growth in these systems is more complicated.

However, the kinetic equations corresponding to step (iii), proposed in [5–7], cannot be regarded as fully satisfactory. In particular, the original approach does not allow to predict the cluster size distribution. Thus, in this Rapid Communication proper kinetic rate equations for the WF mechanism are introduced.

Kinetic rate equations. In order to describe kinetics of step (iii), the approach proposed by Smoluchowski [14, 15], a standard and widely-used tool for description of various coagulation phenomena, is reintroduced [16–29]. In the present case, concentrations of P (c_π), A (c_α), and B_i , (ξ_i), $i \in \mathbb{N}$, are the state variables. Smoluchowski coagulation equations have to be supplemented with the terms related to steps (i), (ii), and (iv). In effect, the time evolution of the system is given by the following rate equations

$$\dot{c}_\pi = -\tilde{k}_\pi c_\pi, \quad (1)$$

$$\dot{c}_\alpha = \tilde{k}_\pi c_\pi - \tilde{k}_\alpha c_\alpha - \sum_{j=1}^{\infty} \tilde{R}_j \xi_j c_\alpha, \quad (2)$$

$$\dot{\xi}_1 = \tilde{k}_\alpha c_\alpha - \tilde{R}_1 \xi_1 c_\alpha - \sum_{j=1}^{\infty} [K_{1j} \xi_1 \xi_j - F_{1j} \xi_{1+j}], \quad (3)$$

$$\begin{aligned} \dot{\xi}_k = & \left(\tilde{R}_{k-1}\xi_{k-1} - \tilde{R}_k\xi_k \right) c_\alpha + \sum_{ij} \frac{1}{2} [K_{ij}\xi_i\xi_j - F_{ij}\xi_k] \\ & - \sum_{j, k+j \leq J} [K_{kj}\xi_k\xi_j - F_{kj}\xi_{k+j}], \quad k > 1, \quad (4) \end{aligned}$$

where $\tilde{k}_\pi \equiv c_\rho k_\pi$, $\tilde{k}_\alpha \equiv c_\rho k_\alpha$, and $\tilde{R}_i \equiv c_\rho R_i$ are observable reaction rate constants for steps (iv), (i), and (ii), respectively, while k_π , k_α , and R_i are the corresponding bare rate constants, and c_ρ is a concentration of the reducing agent, assumed here to be time-independent. $K_{ij} = K_{ji}$ and $F_{ij} = F_{ji}$ denote coagulation and fragmentation kernels. The first sum in (4) is restricted to $i + j = k$.

Initial conditions of interest here are $c_\pi(0) \equiv c_0$, $c_\alpha(0) \equiv d_0$, with $c_0 + d_0 \equiv q_0 \neq 0$, and $\xi_i(0) = 0$, $i \in \mathbb{N}$. The solution for $c_\pi(t)$ is immediate: $c_\pi(t) = c_0 \exp(-\tilde{k}_\pi t)$. The original WF model corresponds to $c_0 = 0$.

It follows that $\dot{c}_\pi(t) + \dot{c}_\alpha(t) + \sum_{j=1}^{\infty} j \dot{\xi}_j(t) = 0$ (mass conservation constraint). Therefore, the quantity

$$q(t) \equiv c_\pi(t) + c_\alpha(t) + \sum_{j=1}^{\infty} j \xi_j(t) = q_0 \quad (5)$$

is conserved during the time evolution.

Apart from the assumption of constant concentration of the reducing agent, $c_\rho(t) = c_\rho(0)$, (A1), it was also assumed that no source term (no injection mechanism) for either P or A species is present (A2); that both the autocatalytic P to A reduction reaction, $P + B_i \rightarrow A + B_i$ (A3), as well as the disproportionation reaction $P + B_1 \longleftrightarrow 2A$ (A4) may be neglected. It was also assumed that neither K_{ij} , nor F_{ij} depend on concentration of c_ρ , c_π or c_α (A5), and finally, that chemical species P, A, and reducing agent (R) do not form clusters (A6). Any of the above assumptions may be abandoned, leading to a generalization of the model defined by Eqs. (2)-(4) [31].

If $\tilde{R}_i = 0$, for all $i \in \mathbb{N}$, (3) and (4) become the standard Smoluchowski equations, with the monomer source term $\tilde{k}_\alpha c_\alpha(t)$ for $\tilde{k}_\alpha \neq 0$. However, for $\tilde{R}_i \neq 0$ such reduction is no longer possible, and Eqs. (1)-(4) with their generalizations are members of a wider class of 'reaction-aggregation' equations. Few models of this type have been found in the literature [26-28].

Method of moments. To analyze properties of Eqs. (2)-(4), it is convenient to apply the standard method of moments. The μ -th moment of the cluster mass distribution is defined as $M_\mu(t) = \sum_{j=1}^{\infty} j^\mu \xi_j(t)$. From Eqs. (3) and (4) we obtain

$$\dot{M}_\mu = \tilde{k}_\alpha c_\alpha + \sum_{j=1}^{\infty} \mathcal{G}_j^{(\mu)} \xi_j c_\alpha + \sum_{p,q} \mathcal{S}_{pq}^{(\mu)} \xi_p \xi_q + \sum_{p=2}^{\infty} \mathcal{T}_p^{(\mu)} \xi_p, \quad (6)$$

where $\mathcal{S}_{pq}^{(\mu)} = \mathcal{S}_{qp}^{(\mu)} \equiv \frac{1}{2}((p+q)^\mu - p^\mu - q^\mu)K_{pq}$, $\mathcal{T}_p^{(\mu)} \equiv \sum_{i=1}^{p-1} (i^\mu - \frac{1}{2}p^\mu)F_{i,p-i}$ and $\mathcal{G}_j^{(\mu)} \equiv [(j+1)^\mu - j^\mu]\tilde{R}_j$.

From Eq. (6) we see, first, that all moments grow due to the monomer production (i), note, $\tilde{k}_\alpha c_\alpha \geq 0$. Secondly, for $\mu = 0$, $\mathcal{G}_j^{(0)} = 0$, because the total cluster concentration M_0 is not affected by autocatalytic reaction (ii). For $\mu = 1$, $\mathcal{S}_{pq}^{(1)} = \mathcal{T}_p^{(1)} = 0$, i.e., the total cluster mass is not changed by coagulation or fragmentation. Thus, for $\mu = 1$, stationary solution of (6) exists for $\tilde{k}_\alpha > 0$. Indeed, for $(\tilde{k}_\alpha + \sum_{j=1}^{\infty} \mathcal{G}_j^{(1)} \xi_j) > 0$, from $\dot{M}_1 = 0$ follows $c_\alpha = 0$. Since $\lim_{t \rightarrow \infty} c_\pi(t) = 0$, Eq. (5) gives $\lim_{t \rightarrow \infty} M_1(t) \equiv \bar{M}_1 = q_0$, as expected for an irreversible reaction. Additionally, for $K_{ij} = F_{ij} = 0$, when $\mathcal{S}_{pq}^{(\mu)} = \mathcal{T}_p^{(\mu)} = 0$, similar procedure proves that all M_μ approach stationary value.

In order to obtain tractable system of time-evolution equations for $M_\mu(t)$ and c_α , a restriction is imposed on μ and F_{ij} so that $\mu \in \mathbb{N} \cup 0$, $F_{ij} \equiv 0$, and \tilde{R}_i and K_{ij} given by

$$K_{ij} = \kappa_0 + \kappa_1(i+j) + \kappa_2 ij, \quad \tilde{R}_i = \tilde{a}_R i + \tilde{b}_R, \quad (7)$$

where \tilde{a}_R , \tilde{b}_R , κ_0 , κ_1 , κ_2 are arbitrary non-negative coefficients. Under these simplifying assumptions, Eqs. (2) and (6) for $\mu = 0, 1, 2$ assume the form

$$\dot{c}_\alpha = \tilde{k}_\pi c_\pi(t) - \tilde{k}_\alpha c_\alpha - \tilde{a}_R M_1 c_\alpha - \tilde{b}_R M_0 c_\alpha, \quad (8)$$

$$\dot{M}_0 = \tilde{k}_\alpha c_\alpha - \frac{1}{2} \kappa_0 M_0^2 - \kappa_1 M_0 M_1 - \frac{1}{2} \kappa_2 M_1^2, \quad (9)$$

$$\dot{M}_1 = \tilde{k}_\alpha c_\alpha + \tilde{a}_R M_1 c_\alpha + \tilde{b}_R M_0 c_\alpha, \quad (10)$$

$$\begin{aligned} \dot{M}_2 = & \tilde{k}_\alpha c_\alpha + [2\tilde{a}_R M_2 + (\tilde{a}_R + 2\tilde{b}_R) M_1 + \tilde{b}_R M_0] c_\alpha \\ & + \kappa_0 M_1^2 + 2\kappa_1 M_1 M_2 + \kappa_2 M_2^2. \end{aligned} \quad (11)$$

The initial conditions, $\forall k : \xi_k(0) = 0$ give $M_\mu(0) = 0$, $\forall \mu$, while variables c_α and M_1 are not independent, since they obey the constraint (5) for $M_1 = \sum_{j=1}^{\infty} j \xi_j(t)$.

Explicit form of the corresponding evolution equations for higher moments ($\mu > 2$) may be easily found using Eq. (6). However, higher moments are not needed to calculate two basic characteristics of the cluster mass distribution, i.e., mean cluster size, $\langle i \rangle$, and variance, $\sigma^2(i)$, as given by

$$\langle i \rangle = \frac{M_1}{M_0}, \quad \sigma^2(i) = \frac{M_2}{M_0} - \left(\frac{M_1}{M_0} \right)^2. \quad (12)$$

Absence of coagulation. The case of negligible coagulation and fragmentation is at the center of our interest. In colloidal systems, experimentally, this is achieved by addition of a stabilizing agent, e.g. the polyvinyl alcohol (PVA) or polyvinylpyrrolidone (PVP), which inhibits coagulation, affecting chemical reactions to a lesser extent [11, 13]. Models of autocatalytic reaction without coagulation may also provide an adequate description for other systems, e.g. simple chain polymers.

For $K_{ij} = F_{ij} = 0$, Eq. (4) divided by Eq. (3) gives

$$\frac{d\xi_k}{d\xi_1} = \frac{\tilde{R}_{k-1}\xi_{k-1} - \tilde{R}_k\xi_k}{\tilde{k}_\alpha - \tilde{R}_1\xi_1}. \quad (13)$$

Eqs. (13) for $k = 2, 3, \dots$ form a system of coupled linear differential equations, allowing to determine each ξ_k as a function of ξ_1 , $\xi_k = s_k(\xi_1)$. If coagulation and fragmentation processes could be neglected, Eqs. (13), therefore all $s_k(\xi_1)$ functions, for given initial conditions, depend only on \tilde{k}_α and \tilde{R}_i parameters, and not on chemical reactions and physical process, e.g. injection of P and A substrates, unless they involve B_i clusters. In particular, $s_k(\xi_1)$, hence the stationary values of ξ_k , $\bar{\xi}_k \equiv \lim_{t \rightarrow \infty} \xi_k(t)$ do not depend on assumptions $\mathcal{A}1$ - $\mathcal{A}3$.

The above holds true for any equation derived by dividing Eq. (3), or one of Eqs. (8)-(11), by Eq. (9) or (10), which allow expressing ξ_1 and M_μ as the functions of M_0 or M_1 only, see Eqs. (18), (26), and (34) below.

As a consequence, all special cases or generalizations of the model defined by Eqs. (1)-(4) with the monomer production provided solely by (i), and with identical mechanism of autocatalytic reaction (ii) belong to the same universality class.

Two special cases of the reaction kernel (7) are analyzed below: the linear kernel, proportional to the cluster mass, $\tilde{R}_i \propto i$, $\tilde{b}_R = 0$; and the size-independent one, $\tilde{a}_R = 0$.

Linear reaction kernel. For $\kappa_0 = \kappa_1 = \kappa_2 = 0$, $\tilde{b}_R = 0$, and $\tilde{a}_R \neq 0$, Eqs. (1), (8), and (10) become identical to the rate equations analyzed in Refs. [12, 13] ($c_0 \neq 0$) and [4-6, 8] ($c_0 = 0$). These equations have the same form for arbitrary choice of K_{ij} and F_{ij} , hence the reaction rate of (ii), proportional to the total mass of the clusters (M_1), does not depend on presence of the coagulation or fragmentation.

c_α may be eliminated in favor of $c_\pi(t)$ and $M_1 \equiv x$ using Eq. (5), which yields the form of Eqs. (10)

$$\dot{x} = (\tilde{k}_\alpha + \tilde{a}_R x) (f(t) - x), \quad (14)$$

where $f(t) \equiv q_0 - c_\pi(t) = d_0 + c_0(1 - \exp(-\tilde{k}_\pi t))$ and $0 \leq x \leq q_0$. The following substitution: $u = \tilde{k}_\alpha + \tilde{a}_R x$ transforms (14) into Bernoulli-type equation, which gives

$$x(t) = \frac{1}{\tilde{a}_R} e^{\Phi(t)} \left(\frac{1}{\tilde{k}_\alpha} + \int_0^t e^{\Phi(\eta)} d\eta \right)^{-1} - \frac{\tilde{k}_\alpha}{\tilde{a}_R}, \quad (15)$$

where $\Phi(t) \equiv C_1(\exp(-\tilde{k}_\pi t) - 1) + C_2 t$, $C_2 = \tilde{a}_R q_0 + \tilde{k}_\alpha$, and $C_1 = c_0 \tilde{a}_R / \tilde{k}_\pi = c_0 k_4 / k_1$. For the original WF model, where $c_0 = 0$, $C_1 = 0$, and $f(t) = d_0 \neq 0$, (15) reduces to

$$x_{\alpha\beta}(t) = - \left(d_0 + \frac{\tilde{k}_\alpha}{\tilde{a}_R} \right) \cdot \left(\frac{\tilde{k}_\alpha}{d_0 \tilde{a}_R} e^{(\tilde{a}_R d_0 + \tilde{k}_\alpha)t} + 1 \right)^{-1} + d_0, \quad (16)$$

where $x_{\alpha\beta}(0) = 0$ and $\lim_{t \rightarrow \infty} x_{\alpha\beta}(t) = d_0$ [4, 12]. However, for $c_0 \neq 0$, $x(t)$ cannot be expressed as a combination of finite number of elementary functions. Still Eq. (15) may be given a more convenient form $x(t) = \chi(z(t))$,

where $z(t) \equiv C_1 \exp(-\tilde{k}_\pi t)$ and $\chi(z)$ is given by

$$\chi(z) = \frac{e^z}{\tilde{a}_R} \left(\left[\frac{e^{C_1}}{\tilde{k}_\alpha} + \frac{{}_1F_1(1-\gamma; 2-\gamma; C_1)}{\tilde{k}_\pi(1-\gamma)} \right] \frac{z^{\gamma-1}}{C_1^{\gamma-1}} - \frac{{}_1F_1(1-\gamma; 2-\gamma; z)}{\tilde{k}_\pi(1-\gamma)} \right)^{-1} - \frac{\tilde{k}_\alpha}{\tilde{a}_R}. \quad (17)$$

Above, $\gamma = 1 + C_2/\tilde{k}_\pi$ and ${}_1F_1(a; b; z)$ denote confluent hypergeometric function [30].

Since in this case, there is an analytic solution (17) for $M_1(t) = x(t)$, it is convenient to express both M_0 and M_2 as the functions of M_1 .

Eq. (9) divided by Eq. (10) gives

$$\frac{dM_0}{dM_1} = \frac{\tilde{k}_\alpha}{\tilde{k}_\alpha + \tilde{a}_R M_1} = \frac{1}{1 + \frac{\omega}{q_0} M_1}, \quad (18)$$

where $\omega = q_0 \tilde{a}_R / \tilde{k}_\alpha = q_0 a_R / k_\alpha$. Eq. (18) gives

$$M_0(M_1) = \frac{q_0}{\omega} \ln \left(1 + \frac{\omega}{q_0} M_1 \right). \quad (19)$$

In parallel, dividing Eq. (11) by Eq. (10) gives

$$M_2(M_1) = M_1 \left(1 + \frac{\omega}{q_0} M_1 \right). \quad (20)$$

Using Eqs. (19) and (20), explicit formulas for mean cluster size and variance (12) may be easily derived.

Solving Eqs. (13) for $\tilde{R}_i = \tilde{a}_R i$ gives

$$\xi_k(t) = s^{(a)}(\xi_1(t)) = \frac{1}{k} \frac{q_0}{\omega} \left(\frac{\omega}{q_0} \xi_1(t) \right)^k, \quad k \geq 1. \quad (21)$$

In order to find $\xi_1(t)$, M_0 (19) is equated with $\sum_{j=1}^{\infty} \xi_j(t)$. Employing (21) and the identity

$$\sum_{k=1}^{\infty} \frac{x^k}{k} = \ln \left(\frac{1}{1-x} \right) = \ln \left(1 + \frac{x}{1-x} \right), \quad (22)$$

where $x = \Omega \cdot (\Omega + 1)^{-1}$ and $\Omega = \omega M_1 / q_0$, gives

$$\xi_1(t) = h_1^{(a)}(M_1(t)) = \frac{M_1(t)}{1 + \frac{\omega}{q_0} M_1(t)}. \quad (23)$$

Combining Eqs. (21) and (23), the following is found

$$\bar{\xi}_k \equiv \lim_{t \rightarrow \infty} \xi_k(t) = \frac{1}{k} \frac{q_0}{\omega} \left(\frac{\omega}{\omega + 1} \right)^k. \quad (24)$$

Finally, for $c_0 = 0$, Eqs. (16), (21) and (23) yield

$$\xi_k^{(\alpha\beta)}(t) = \frac{1}{k} \frac{d_0}{\omega} \left(\frac{\omega}{\omega + 1} \right)^k \left(1 - e^{-\tilde{k}_\alpha(1+\omega)t} \right)^k. \quad (25)$$

Size-independent reaction kernel. For colloidal systems, \tilde{R}_j given by Eq. (7), for $\tilde{a}_R = 0$ and $\tilde{b}_R \neq 0$,

provides a lower bound for any realistic functional form of \tilde{R}_j , which is expected to be a non-decreasing function of j . Moreover, in the absence of coagulation, i.e., for $\kappa_0 = \kappa_1 = \kappa_2 = 0$, Eqs. (8)-(11) may be regarded as a simple model of linear polymer growth [32], cf. [28]. In this case, to solve Eqs. (8)-(11), Eq. (10) is divided by Eq. (9), giving

$$\frac{dM_1}{dM_0} = 1 + \frac{\tilde{b}_R}{\tilde{k}_\alpha} M_0 = 1 + \frac{\omega}{q_0} M_0, \quad (26)$$

where $\omega \equiv q_0 \tilde{b}_R / \tilde{k}_\alpha = q_0 b_R / k_\alpha$. Eq. (26) gives

$$M_1(M_0) = \frac{\omega}{2q_0} M_0^2 + M_0. \quad (27)$$

Applying a parallel procedure to Eqs. (11) and (9), with the use of $M_1(M_0)$ (27), and solving the equation gives

$$M_2(M_0) = M_0 + \frac{3\omega}{2q_0} M_0^2 + \frac{\omega^2}{3q_0^2} M_0^3. \quad (28)$$

Using Eqs. (27), (10) and the constraint (5) in order to eliminate c_α , yields the following equation

$$\dot{M}_0 = \tilde{k}_\alpha \left(q_0 - c_\pi(t) - M_0 - \frac{\omega}{2q_0} M_0^2 \right). \quad (29)$$

For $c_0 \neq 0$, it was impossible to find an analytical solution of Eq. (29). However, the stationary solution of Eq. (29) may easily be found. Combining Eq. (27) and the limit $\lim_{t \rightarrow \infty} M_1 = q_0$, gives

$$\lim_{t \rightarrow \infty} \left[M_0(t) + \frac{\omega}{2q_0} M_0^2(t) \right] = \bar{M}_0 + \frac{\omega}{2q_0} \bar{M}_0^2 = q_0. \quad (30)$$

Eq. (30) implies

$$\bar{M}_0 = \frac{q_0}{\omega} (\sqrt{1 + 2\omega} - 1). \quad (31)$$

Eq. (29) may also be easily solved for $c_0 = 0$, giving

$$M_0(t) = \frac{d_0}{\omega} \cdot \frac{(\eta - 1) (1 - e^{-\tilde{k}_\alpha \eta t})}{1 + \left(\frac{\eta - 1}{\eta + 1} \right) e^{-\tilde{k}_\alpha \eta t}}, \quad (32)$$

where $\eta \equiv \sqrt{1 + 2\omega}$. $M_0(t)$ (32) has the following properties: $M_0(0) = 0$, $M_0(t) < \bar{M}_0$, where \bar{M}_0 is given by (31) and $\lim_{t \rightarrow \infty} M_0(t) = \bar{M}_0$, as might have been expected. Eqs. (27), (28), and (32) may be used to calculate the time-dependence of $\langle i \rangle_p$ and $\sigma^2(i)$ (12).

For $\tilde{R}_i = \tilde{b}_R$, solutions of Eqs. (13) read

$$\xi_k = s^{(b)}(\xi_1) = \frac{q_0}{\omega} \left\{ 1 + u(\xi_1) W_{k-1} \left[\ln \left(\frac{-1}{u(\xi_1)} \right) \right] \right\}, \quad (33)$$

where $u(\xi_1) = \frac{\omega}{q_0} \xi_1 - 1$ and $W_i(x) \equiv \sum_{j=0}^i x^j / j!$, which may be easily verified (note, $W_{k-1}(x) = W'_k(x)$). To

obtain explicit form of $\xi_1(t)$, Eq. (13) is divided by Eq. (9). This yields

$$\frac{\dot{\xi}_1}{M_0} = \frac{d\xi_1}{dM_0} = 1 - \frac{\omega}{q_0} \xi_1. \quad (34)$$

The solution of Eq. (34) is given by

$$\xi_1(t) = h_0^{(b)}(M_0(t)) = \frac{q_0}{\omega} \left(1 - e^{-\frac{\omega}{q_0} M_0(t)} \right), \quad (35)$$

where for $c_0 = 0$, $M_0(t)$ is given by (32).

Using Eqs. (31), (33), and (35), stationary value of each ξ_k may easily be found

$$\bar{\xi}_k \equiv \lim_{t \rightarrow \infty} \xi_k = \frac{q_0}{\omega} \left[1 - e^{-(\eta-1)} W_{k-1}(\eta-1) \right]. \quad (36)$$

Finally, for the cluster size-independent reaction kernel, coagulation process, when present, decrease the rate of the autocatalytic reaction (ii). This becomes intuitively clear, when the present model is applied to describe growth of linear polymers with two active reaction sites at the ends of the polymer chain, since each coagulation event reduces the number of reaction sites by a factor two. Clearly, the influence of fragmentation processes is exactly opposite.

Summary and discussion. In this paper, time-evolution rate equations for the model of transition-metal nanocluster formation, as proposed by Watzky and Finke, have been introduced. The equations introduced constitute a natural generalization of both the Smoluchowski coagulation equations, and the rate equations, describing the kinetics of monomer production, autocatalytic nanoparticle surface growth, and other chemical reactions present in the system.

In the absence of coagulation and fragmentation, exact solutions of the model equations have been found for the autocatalytic rate constant (reaction kernel) proportional to cluster mass, $\tilde{R}_i \propto i$, as well as for the cluster-size independent one, $\tilde{R}_i = \text{const}$.

Secondly, it was demonstrated that the functional dependence of the k -atom cluster concentrations, ξ_k on ξ_1 , given by $\xi_k = s(\xi_1)$, and $\bar{\xi}_k \equiv \lim_{t \rightarrow \infty} \xi_k(t)$, are completely determined by the assumed model mechanism of monomer production and autocatalytic growth, but do not depend on any other chemical reaction. However, this does not hold for the $\xi_k(t)$ functions.

In conclusion, kinetically inequivalent generalizations of the present model are divided into universality classes, whereby two such models belong to the same class when they yield the same $s(\xi_1)$ function.

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- [31] An article is in preparation, proposing a model with assumptions (A1)-(A6) abandoned.
- [32] In this case, A denotes an 'active monomer', while B₁ is an 'inert' or 'inactive monomer' which cannot take part in the polymerization process.